

Heat Capacity of $\text{Na}_{0.3}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$, a New Two-Gap Superconductor: Comparison with the Heat Capacity of MgB_2

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The superconducting-state heat capacity of $\text{Na}_{0.3}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ shows unusual, marked deviations from BCS theory, at all temperatures. At low temperatures the heat capacity has the T^2 dependence characteristic of line nodes in the energy gap, rather than the exponential temperature dependence of a fully gapped, conventional superconductor. At temperatures of the order of one fifth of the critical temperature and above, the deviations are strikingly similar to those of MgB_2 , which are known to be a consequence of the existence of substantially different energy gaps on different sheets of the Fermi surface. A two-gap fit to the $\text{Na}_{0.3}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ data gives gap amplitudes of 45% and 125% of the BCS value, on parts of the Fermi surface that contribute, respectively, 45% and 55% to the normal-state density of states. The temperature of the onset of the transition to the vortex state is independent of magnetic field, which shows the presence of unusually strong fluctuations.

INTRODUCTION

Among the unusual superconductors discovered in recent years, two, MgB_2 in 2001 [1] and $\text{Na}_{0.3}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ in 2003 [2], are superconducting at ambient pressure. Both are of special interest in connection with unusual features of the electron-pairing mechanism, and in both cases the heat capacity (C) shows unusual, strong deviations from BCS theory [3] that are related to these features. At temperatures (T) that are well below the critical temperature (T_c) the deviations are different in the two cases, and suggest a difference in the electron pairing; at intermediate and high temperature the deviations are very similar, and show the presence of two distinctly different energy gaps.

The BCS theory of 1957 showed that high values of T_c were favored by small atomic mass. Given the ensuing search for superconductivity in compounds of light elements, including B, and the commercial availability of MgB_2 for many years, the late date of the (apparently accidental) discovery of superconductivity in MgB_2 was itself a surprise. However, the initial intense interest generated by the discovery derived from the fact that, although the isotope effect [4] suggested that MgB_2 was a "conventional" BCS superconductor with phonon-mediated electron pairing, $T_c = 39$ K seemed too high for that mechanism. The BCS phonon mechanism has been confirmed by theoretical work [5, 6, 7, 8, 9, 10], which, in concert with a variety of experimental measurements including heat-capacity measurements, has also shown that MgB_2 is an example of multi-gap superconductivity. The possibility of multi-band, multi-gap superconductivity had been recognized theoretically [11] in 1959 and a number of the properties predicted [11, 12], but MgB_2 is the first example to show the properties so clearly and in such detail. For the superconducting-state, conduction-electron contribution (C_{es}) to C the relevant theoretical predictions for a two-gap superconductor are: 1) for any realistic interband coupling the two gaps will open at a common T_c ; 2) one gap must be smaller than the BCS gap and the other greater; 3) at low temperature C_{es} is determined by the small gap; 4) the discontinuity in C_{es} at T_c is smaller than the BCS value. For MgB_2 , C_{es} conforms to all of these predictions and is accurately represented by a two-gap model that is in quantitative agreement with both spectroscopic measurements [13] and theoretical calculations [8, 9, 10]. MgB_2 is well established as a two-gap superconductor, and C_{es} can be taken as a model for comparison with other superconductors that might have more than one gap.

The superconductivity of $\text{Na}_{0.3}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ is of particular interest for comparison with that of the cuprates: The 1986 discovery [14] of superconductivity in the layered perovskite cuprates, for which T_c reaches 133 K [15], raised the question of whether high- T_c superconductivity might be found in similar structures with transition-metal ions other than Cu. Co was recognized as an interesting candidate almost immediately, but the superconductivity of $\text{Na}_{0.3}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$, with a relatively low T_c , about 5 K, was not discovered until 2003 [2]. In the cuprates the Cu ions are in corner-sharing O octahedra or pyramids, in an approximately square array. In the parent undoped Mott insulator the Cu ions are ordered antiferromagnetically, and antiferromagnetic spin fluctuations are thought to have a role in the electron pairing in the hole-doped superconducting phases. In $\text{Na}_{0.3}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ the Co ions are at the centers of *edge*-sharing O octahedra, in a *triangular* array, which produces frustration of the antiferromagnetic interaction that is expected to affect the superconductivity.

Theoretical work suggests that the electron pairing in $\text{Na}_{0.3}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ is "unconventional", and perhaps unique.

Experimental work has been limited by the complicated synthetic procedures, the sensitivity of the superconductivity to stoichiometry, and the relative instability of the superconducting material. Only a few measurements that give clues to the nature of the pairing state have been made, and some of the results are contradictory: NQR and NMR spin-lattice relaxation rates [16] and μ SR measurements [17] suggest line nodes in the energy gap, but a coherence peak in NQR measurements suggests an isotropic gap [18]. C_{es} gives information about the symmetry of the gap: For conventional superconductors an exponential decrease of C_{es} corresponds to a fully gapped Fermi surface. For a superconductor with nodes in the gap a power-law temperature dependence is expected, with the exponent determined by the form of the nodes. Point nodes give $C_{es} \propto T^3$; line nodes give $C_{es} \propto T^2$. A number of heat-capacity measurements have been reported [19, 20], but in many cases the interpretation of the data has been limited by substantial contributions from magnetic impurities or a lack of low-temperature data. New measurements of the heat capacity of $\text{Na}_{0.3}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$, from 0.8 to 33 K and in magnetic fields (B) to 9 T, are reported here and compared with previously published results for MgB_2 .

HEAT CAPACITY OF MgB_2

Several measurements of the heat capacity of MgB_2 show the presence of excitations at energies below the gap energy of a BCS superconductor, i.e., a second small gap on a part of the Fermi surface [21, 22]. Figure 1 shows comparisons of C_{es} data [22] with a two-gap model [23] and with the BCS theory for the weak-coupling limit, as $C_{es}/\gamma T$ vs T/T_c , where γ is the coefficient of the conduction-electron, normal-state contribution ($C_{en} = \gamma T$) to C . (For this sample $T_c = 38.9$ K and $\gamma = 2.53$ mJ mol $^{-1}$ K $^{-2}$.) Near T_c , where the BCS curve has negative curvature, the data show positive curvature, which is characteristic of strong coupling. However, for strong-coupling superconductors the discontinuity in C_e at T_c is generally greater than the BCS value; in this case it is less. This apparent discrepancy is resolved when there are two gaps on different sheets of the Fermi surface that make additive contributions to C_{es} : The large gap determines the *shape* of C_{es} near T_c but the *magnitude* of that contribution is reduced by the fractional contribution of that sheet to γ , γ_1/γ , and the small-gap sheet makes only a small contribution to C_{es} near T_c . Below $T_c/2$, $C_{es}/\gamma T$ is greater than the BCS values, by orders of magnitude at the lowest temperatures. This excess contribution shows the presence of excitations at energies below that of the BCS gap, i.e., excitations across the small gap. These features in C_{es} are well described by a two-gap fit [23], as shown in Fig. 1. That fit is based on the α model [24], a semi-empirical extension of the BCS thermodynamics to strong-coupling superconductors. In the weak-coupling limit of the BCS theory the 0-K gap parameter, $\Delta(0)$, is given by $\Delta(0)/k_B T_c = 1.764$. For a strong-coupling superconductor $\Delta(0)/k_B T_c > 1.764$, and in the α model that ratio is taken as an adjustable parameter, $\alpha \equiv \Delta(0)/k_B T_c$. For a strong-coupling superconductor the temperature dependence of the gap parameter, $\Delta(T)$, can be different from that of the weak-coupling limit, but in the α model it is approximated by the same temperature dependence. The model gives the thermodynamic properties of superconductors with thermodynamic consistency. For strong-coupling superconductors (e.g., Pb, for which the experimental value of α is 2.4) it gives the thermodynamic properties in agreement with experiment, suggesting that the approximation used in the temperature dependence of $\Delta(T)$ is not a serious shortcoming. For a single-gap superconductor a value of α less than that of the weak-coupling limit would be physically unrealistic, but for one of the gaps of a two-gap superconductor it is thermodynamically required. In Fig. 1, C_{es} is represented as the sum of contributions from two sheets of the Fermi surface with different values of α , weighted by their fractional contributions to γ , γ_1/γ and γ_2/γ . The curve for each contribution makes its role in determining the overall temperature dependence of C_{es} clear. This interpretation of the heat capacity of MgB_2 , including the values of the three adjustable parameters, α_1 , α_2 , and γ_1/γ_2 , is in good agreement with a number of spectroscopic measurements [13] and theoretical calculations [8, 9, 10]. The two-gap nature of MgB_2 is thus well established.

HEAT CAPACITY OF $\text{Na}_{0.3}\text{COO}_2 \cdot 1.3\text{H}_2\text{O}$

$\text{Na}_{0.3}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ was prepared by chemical de-intercalation of sodium from $\text{Na}_{0.75}\text{CoO}_2$ and subsequent washing with water [25]. A 0.5-g sample of the resulting powder was placed in a Au-plated Cu container with excess water and lightly pressed to promote thermal contact. The heat capacity was measured with a heat-pulse technique. The amount of $\text{Na}_{0.3}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ in the water/sample mixture was determined by chemical analysis. The data were corrected for the contributions of the container (calculated) and the excess water (from published values of the heat capacity [26]).

The heat capacity is shown as C/T in Fig. 2 for $B = 0$ and 9 T. The anomaly at 4.5 K in the zero-field data

marks the transition to the superconducting state. The low-temperature upturn in the 9-T data is a T^{-2} hyperfine contribution. The 9-T data do not show the evidence of a transition to the vortex state that is apparent in the data for all other fields (see Fig. 6). Evidently the sample is normal to the lowest temperature in 9 T, and B_{c2} is approximately 9 T. After subtraction of the T^{-2} term, γ and the lattice contribution to the heat capacity (C_l) were determined by fitting the 9-T data below 12 K and the zero-field data between 6 and 12 K with the expression $C = C_{en} + C_l = \gamma T + B_3 T^3 + B_5 T^5 + B_7 T^7$. The fit gave $\gamma = 16.10 \text{ mJ mol}^{-1} \text{ K}^{-2}$, near the high end of the range of published values, which vary by about 30% [19, 20], and $B_3 = 0.126 \text{ mJ mol}^{-1} \text{ K}^{-4}$, at the low end of the range of published values, which vary by a factor of five. The wide range of reported values of B_3 may be due to inadequate corrections for the contribution of excess water.

There is also a small T^{-2} upturn in the zero-field data, which is barely visible in Fig. 2. It could arise from a low concentration of weakly interacting paramagnetic centers, but the absence of Schottky anomalies in any of the in-field measurements (see particularly Figs. 2 and 3 where the zero-field and 9-T data are essentially indistinguishable above 6 K) shows that the concentration is too low to have a significant effect on the interpretation of the data. Another possibility is that it is a hyperfine contribution from a magnetic impurity in the container. Apart from the small T^{-2} term, the lowest-temperature, zero-field data are linear in T . An extrapolation of this temperature dependence to 0 K gives the correct entropy at 6 K, which supports its validity. The extrapolation also gives a non-zero intercept at 0 K, a normal-state-like residual γ , $\gamma_r = 6.67 \text{ mJ mol}^{-1} \text{ K}^{-2}$. All heat-capacity measurements on this material show evidence of a contribution of this type, and we make the usual interpretation, which is that a fraction of the sample, $\gamma_r/\gamma = 0.41$, does not become superconducting. For each field except 9 T the electron contribution to the heat capacity (C_e) was calculated by subtracting $\gamma_r T$, C_l , and the T^{-2} term from C , and scaling the result to correspond to one mole of superconducting material. The results for 0 and 9 T, $C(9 \text{ T}) = C_{en}$ and $C(0) = C_{es}$, are shown in Fig. 3. The entropy-conserving construction on C_{es} gives a discontinuity, $\Delta C_{es}(T_c)/T_c = 13 \text{ mJ mol}^{-1} \text{ K}^{-2}$ at $T_c = 4.52 \text{ K}$. At low temperatures C_{es} shows the T^2 dependence characteristic of line nodes in the gap, not the exponential temperature dependence of a fully-gapped conventional superconductor. The same conclusion has been reported by Yang et al. [20].

In Fig. 4, C_{es} data for both $\text{Na}_{0.3}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ and MgB_2 are compared with BCS theory. Above $T/T_c = 0.2$ the experimental results, and their deviations from BCS theory, are remarkably similar. Given the unusual nature of these deviations from BCS theory, and the well established explanation of their origin in MgB_2 as a manifestation of two different energy gaps, they show that $\text{Na}_{0.3}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ is another two-gap superconductor. A two-gap fit to the $\text{Na}_{0.3}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ data, similar to that for MgB_2 in Fig. 1, is shown in Fig. 5. The major difference between the two fits, which is required by the fact that the α model is based on BCS thermodynamics and cannot represent the effect of nodes in the gap, is that the fit for $\text{Na}_{0.3}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ is made only for $T/T_c \geq 0.4$. The dotted extension of the small-gap contribution below $T/T_c = 0.4$ is just the difference between the experimental data and the extrapolated large-gap contribution. However, the small-gap contribution determined in this way, including the extension below $T/T_c = 0.4$, is very similar to the contribution of a part of the Fermi surface with a small gap and line nodes in Sr_2RuO_4 [27].

The vortex-state results, shown in Fig. 6, give evidence of unusual strong fluctuation effects, possibly related to an unusual pairing mechanism. In most superconductors the onset temperature of the transition to the vortex state is reduced with increasing field. For $\text{Na}_{0.3}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$, to within the precision of the data, it is the same in all fields. Fluctuations do broaden the transition to the vortex state, but the magnitude of the effect in $\text{Na}_{0.3}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ seems to be without precedent, even greater than in the cuprates, the first superconductors in which it was observed. The extrapolations of the vortex-state C_e to 0 K define the magnetic field dependence of the coefficient of the temperature-proportional term, $\gamma(B)$, which is shown in the inset to Fig. 6, and compared with that for MgB_2 in Fig. 7. The sharp initial increase in γ with increasing field for MgB_2 is associated with the closing of the small gap in small fields. For $\text{Na}_{0.3}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$, γ is almost linear in field and the deviations from linearity are on the order of what might be expected from anisotropy of B_{c2} . This difference in behavior is apparently another manifestation of the line nodes in the gap.

CONCLUSION

$\text{Na}_{0.3}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ is another two-gap superconductor, with gaps that are approximately 45% and 125% of the BCS values. The parameters characterizing the two parts of the Fermi surface with different gaps are remarkably similar to those for MgB_2 . In contrast with MgB_2 , however, the low-temperature, superconducting-state heat capacity has a T^2 dependence that shows the presence of line nodes in the small gap, and unconventional superconductivity. The field independence of the onset temperature of the transition to the vortex state shows the presence of unprecedented

strong fluctuation effects, which may be associated with a novel pairing state.

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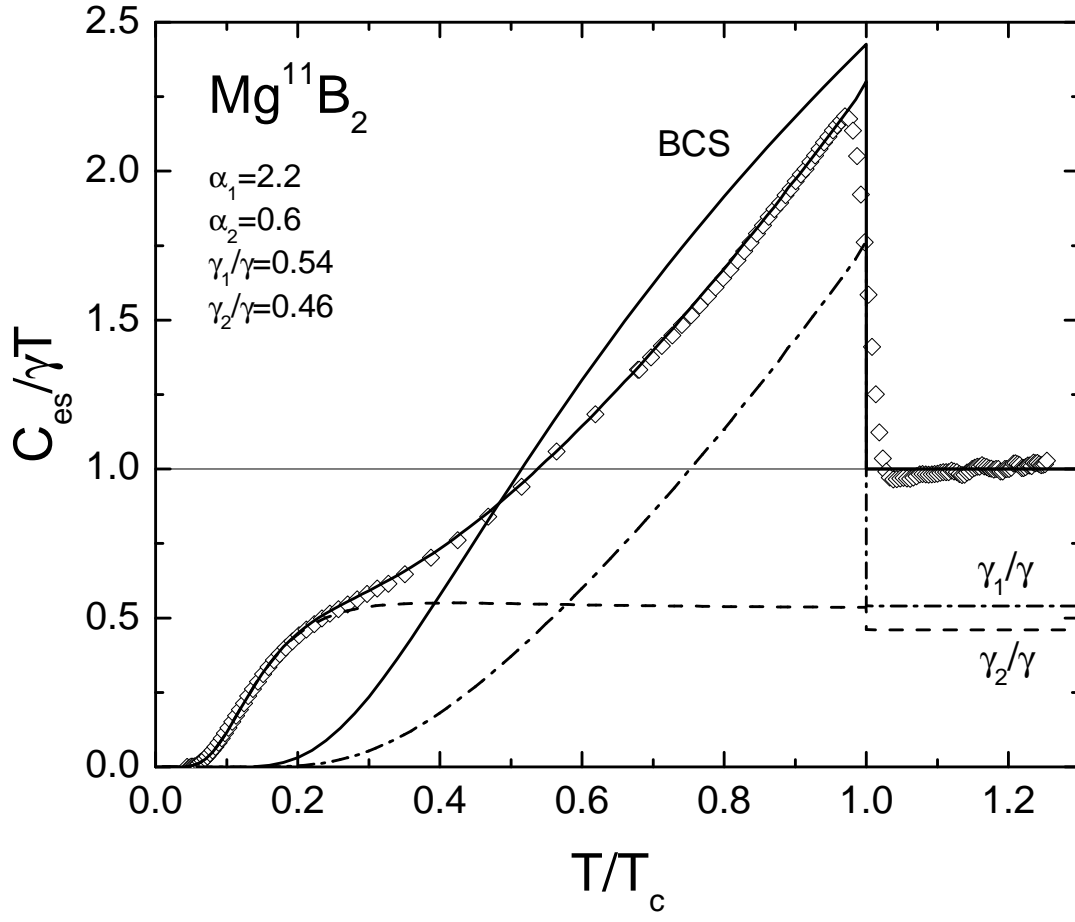


FIG. 1: Conduction-electron, superconducting-state heat capacity of MgB_2 compared with BCS theory and a two-gap model.

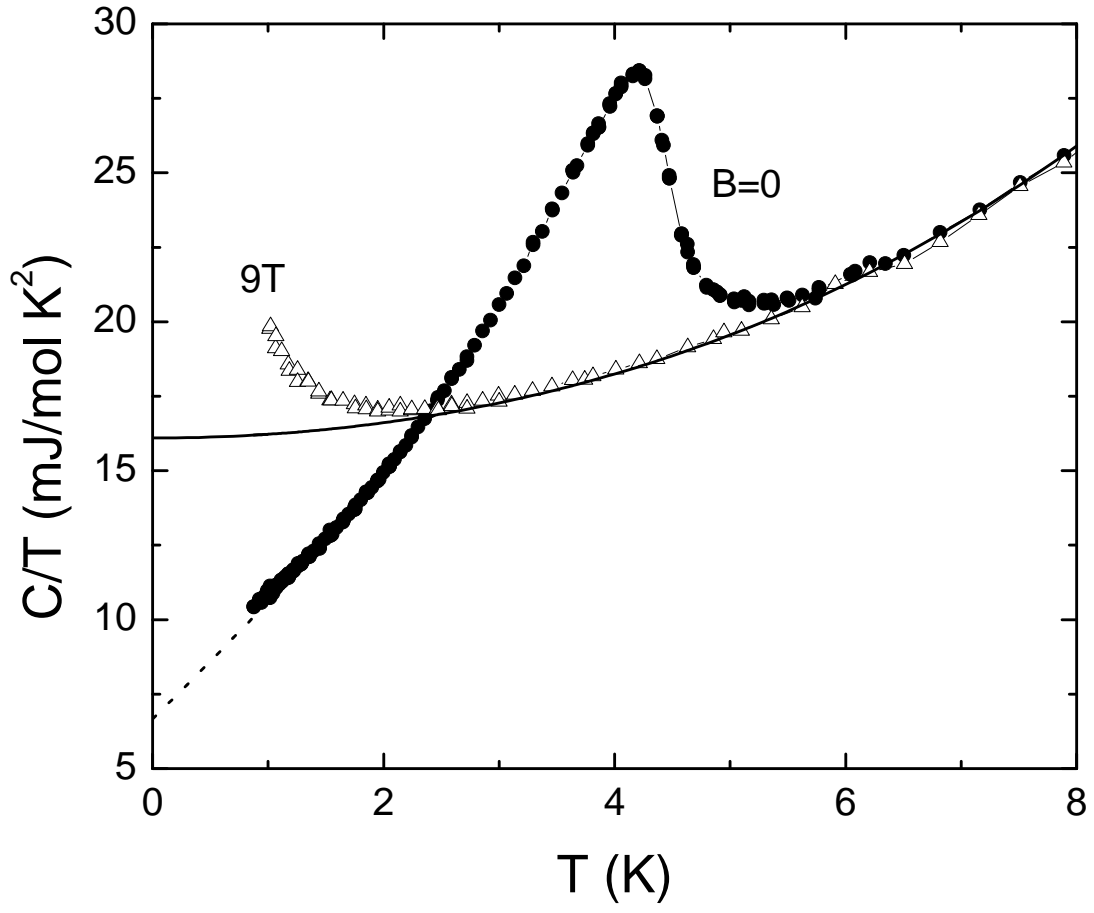


FIG. 2: Heat capacity of $\text{Na}_{0.3}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ in 0 and 9 T.

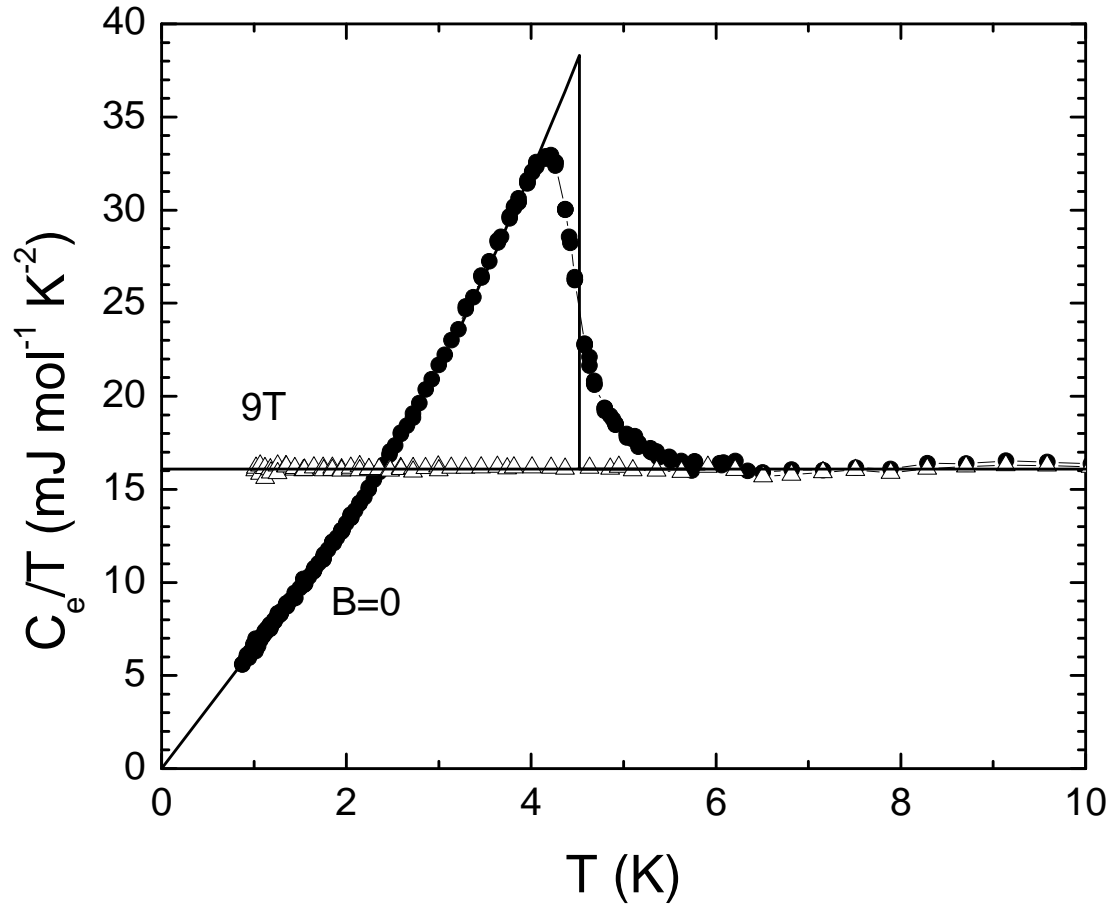


FIG. 3: Electron contribution to the heat capacity of $\text{Na}_{0.3}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ in 0 and 9 T.

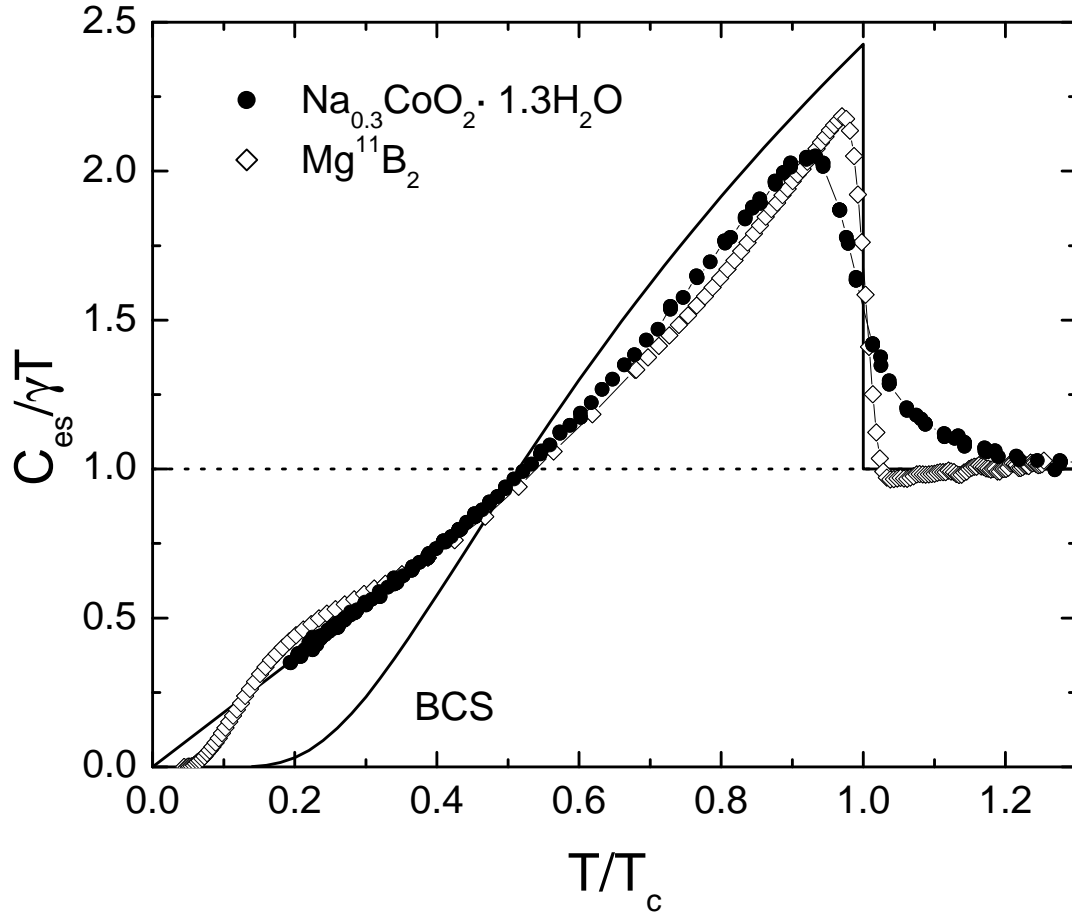


FIG. 4: Deviations of the heat capacities of MgB_2 and $\text{Na}_{0.3}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ from BCS theory.

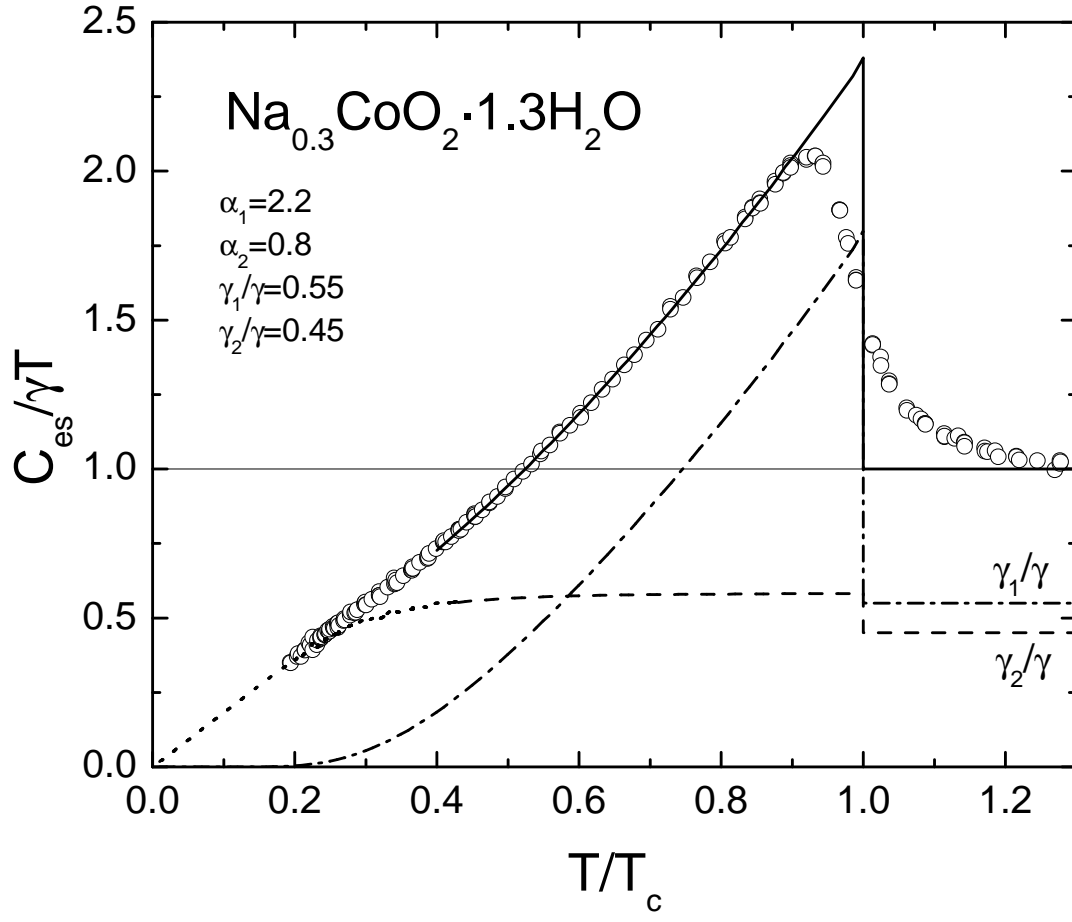


FIG. 5: A two-gap fit to the heat capacity of Na_{0.3}CoO₂·1.3H₂O.

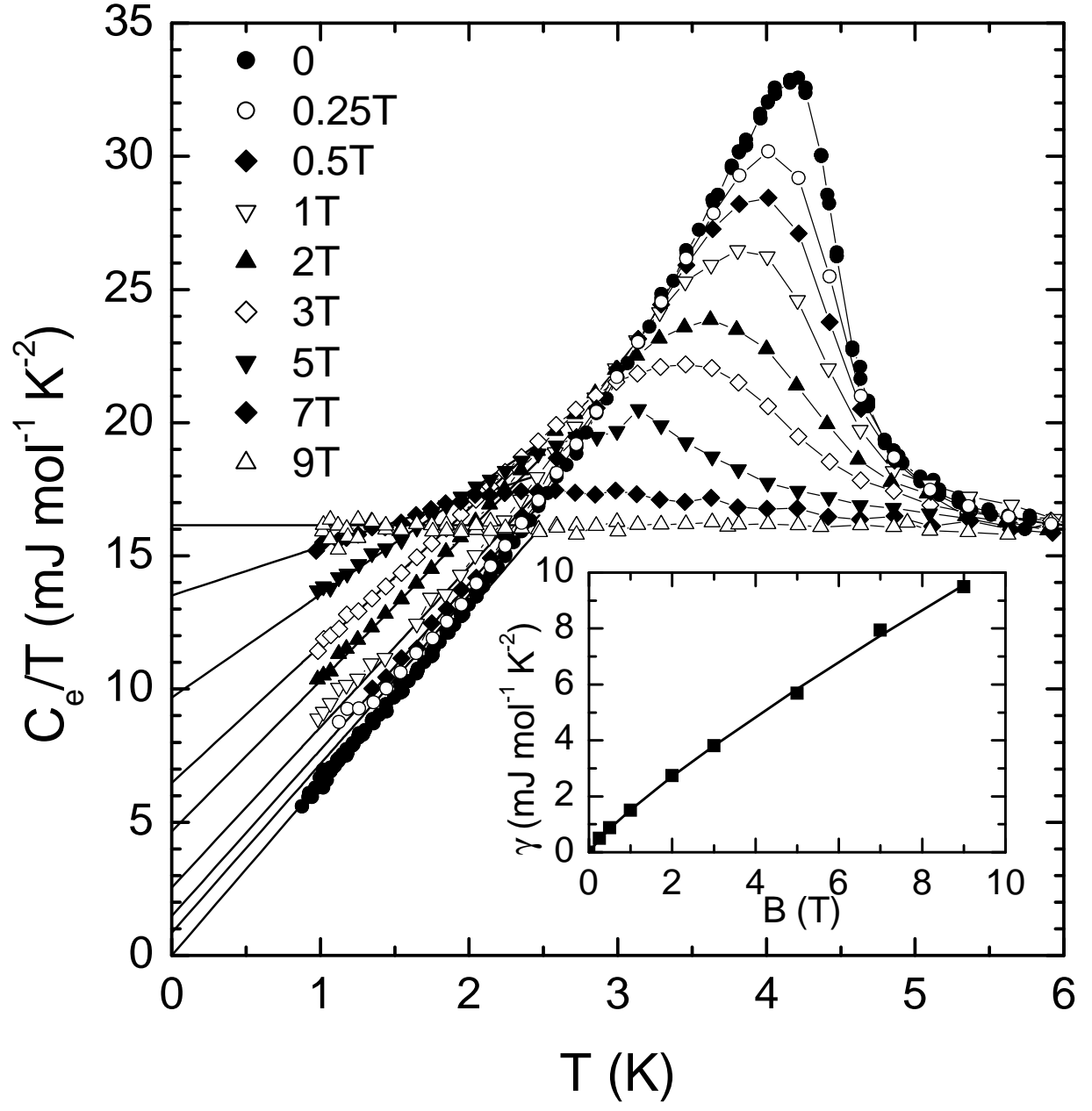


FIG. 6: Vortex-state heat capacity of $\text{Na}_{0.3}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$. The inset shows the magnetic field dependence of the temperature-proportional term.

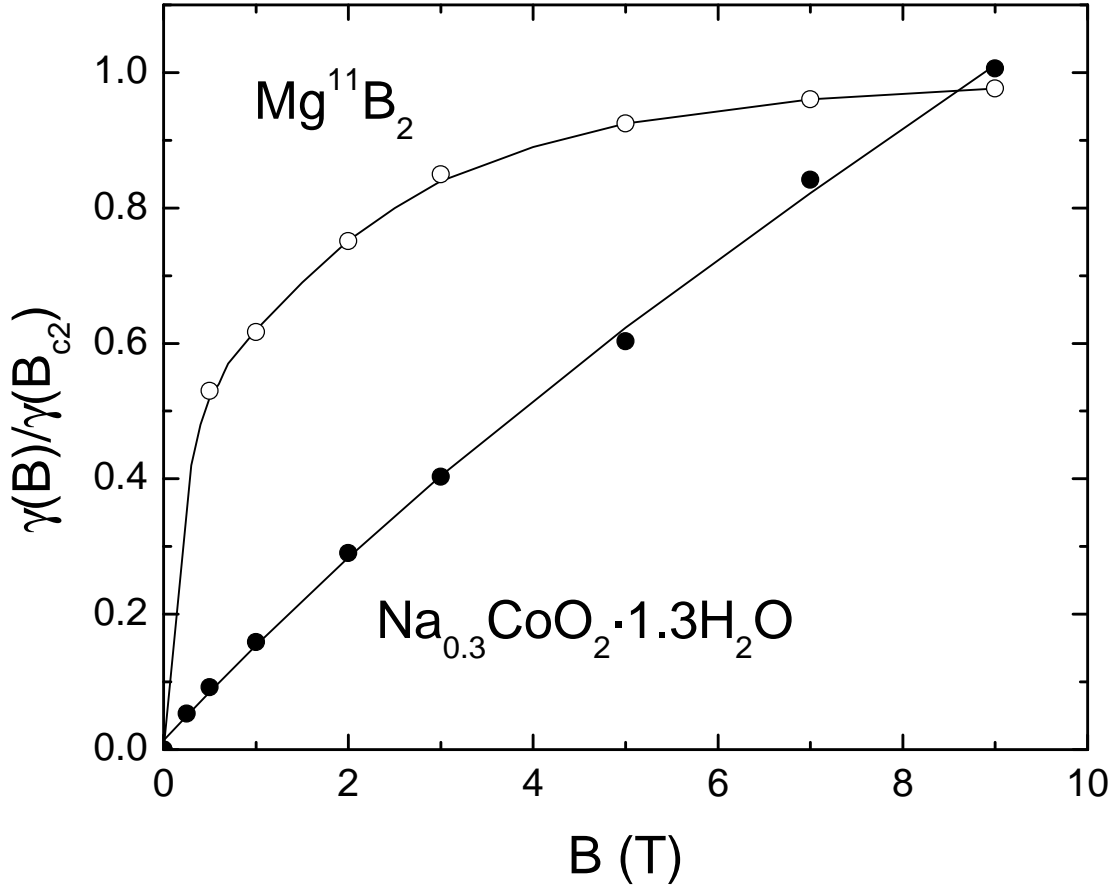


FIG. 7: Comparison of γ in the vortex state for MgB₂ and Na_{0.3}CoO₂·1.3H₂O.